



Research and Development

CAPSTONE REPORT ON THE
DEVELOPMENT OF A STANDARD TEST
METHOD FOR VOC EMISSIONS FROM
INTERIOR LATEX AND ALKYD PAINTS

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Capstone Report

on the Development of a Standard Test Method for VOC Emissions from Interior Latex and Alkyd Paints

by
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Abstract

This document provides a detailed report on the small-chamber test method developed by EPA/NRMRL for characterizing volatile organic compound (VOC) emissions from interior latex and alkyd paints. Current knowledge about VOC, including hazardous air pollutant, emissions from interior paints generated by tests based on this method are presented. Experimental data were analyzed to demonstrate the usefulness of the method and test results in terms of emission characterization, material selection, exposure assessment, and emission reduction by product reformulation. The conclusions drawn from the experimental results were used as input to develop a standard practice to be adopted by the American Society of Testing and Materials (ASTM). The draft standard practice is presented in Appendix A.

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Executive Summary and Conclusions

Americans spend about 90% of their time indoors, where concentrations of pollutants are often much higher than they are outdoors. It is not surprising, therefore, that risk assessment and risk management studies have shown that indoor environmental pollution poses significant risks to human health.

The U.S. Environmental Protection Agency (EPA) has evaluated a number of indoor materials and products as potential sources of indoor air pollution under the Indoor Air Source Characterization Project (IASCP). Interior architectural coatings, especially alkyd and latex paints, were identified as potentially high-risk indoor sources by the Source Ranking Database developed under the IASCP. EPA conducted a literature survey and found that there was a lack of reliable and consistent paint emission data for developing and evaluating risk management options. Further investigation showed that a standardized test method needed to be developed so that testing laboratories, researchers, and paint manufacturers could generate and report emission data that were complete, consistent, and comparable.

Between 1995 and 1999, EPA's National Risk Management Research Laboratory (NRMRL) conducted a paint emission characterization research program. The program was devoted to developing, verifying, and demonstrating a small chamber test method for the measurement of volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions from alkyd and latex paints. The test method has been documented and submitted to the American Society for Testing and Materials (ASTM) for adoption as a standard practice.

This report summarizes the resulting test method, presents new findings, and describes the key results generated by NRMRL as it assessed emissions from alkyd and latex paints. The report is divided into four parts. After introducing the study and providing background information about existing literature on the subject paint emissions testing, the report describes the developed standard test method for characterizing organic compounds emitted from paint. It also describes the results of NRMRL's tests on alkyd and latex paints.

Standardized Test Method

The standardized test method addresses the following key issues:

- Storing and handling paint samples prior to analysis
- Analyzing paint in bulk (as a liquid)
- Selecting and preparing a paint substrate for testing
- Applying paint to a substrate to create a test specimen

- Establishing and controlling test conditions
- Sampling the VOC emissions from the painted specimen
- Analyzing the samples with chemical instruments
- Calculating emission rates/factors using experimental data
- Conducting quality assurance/quality control

The core experimental apparatus employed by the standardized test method is a device called a Small Environmental Test Chamber (“small chamber” for short). A test chamber is a hollow box that may range in size from a few liters to 5 m³. The chamber used at NRMRL is 53 L (0.053 m³) in volume. Chambers with volumes greater than 5 m³ are defined as “large”—they may reach the scale of an entire room. The small chamber, on the other hand, is an apparatus suited to the spatial and financial constraints of a typical laboratory environment. It is also more convenient to operate than a large chamber. An environmental chamber test facility designed and operated to determine organic emission rates from paints should contain the following: test chambers, clean air generation system, monitoring and control systems, sample collection and analysis equipment, and standards generation and calibration systems. The purpose of these components is to provide a controlled environment for conducting emissions testing that can reflect common indoor air conditions.

The standardized test method includes a series of procedures and guidelines for preparing a painted test specimen. Procedures for handling and storing the paint to be tested were established to guard against the possibility of evaporative losses, stratification, and property changes. A modified version of EPA Method 311 (40 CFR, 1996) was adopted for the bulk analysis of paints, to facilitate the experimental design of the emissions test and the selection of sampling and analytical techniques. Instead of traditional test substrates such as glass, stainless steel, and aluminum, common indoor materials such as gypsum board and wood are recommended in the method for creating realistic and representative testing samples. Either a roller or a brush should be used to apply the paint to the substrate. A protocol was developed to quantify the amount of the paint applied so that the emission data can be consistent and comparable.

The “time zero” for the start of an emission test is established when the chamber door is closed (immediately after placing the test specimen inside the chamber). The small chamber should be operated to match the actual environmental conditions at which people paint the interiors of houses. The standardized method guides investigators in setting up their sampling protocols. The instructions help to ensure that investigators collect an adequate quantity of chamber air samples on the appropriate sampling media. The method describes several kinds of analytical instruments that can be used to determine the amounts and kinds of VOCs in the collected sample. Data reduction techniques and an example of an emission model are included in the method—it describes the mathematical procedures used to convert the analytical results into emission rates and emission factors. In addition, the method provides guidelines for reporting and quality assurance. These guidelines should help investigators compile their results in a consistent and

complete fashion that allows for comparison or repeat emissions testing of similar or new architectural coatings.

Alkyd Paints

Alkyd paint continues to be used indoors because it has desirable properties such as durability, gloss, gloss retention, and fast drying. NRMRL has employed the developed standardized test method to conduct research that characterizes VOC emissions from alkyd paint. NRMRL used the results of its paint emissions tests to develop source emission models. These models, in turn, were used for the assessment of indoor exposure levels and risk management options.

The first test series that NRMRL performed on alkyd paints was integrated into the process of developing and validating its new standard practices for paint testing. The tests involved one primer and three alkyd paints. Bulk analysis indicated that the alkyd primer and two of the three paints tested contained more than 100 different VOCs, primarily straight-chain alkanes, with decane and undecane being the predominant compounds. The third paint had more branched alkanes. All four coatings contained low levels of aromatic compounds. The total VOC content of the liquid paints ranged from 32% to 42%. Measurements of the total VOC levels in the liquid coatings by gas chromatography/mass spectrometry (GC/MS) agreed well with manufacturers' data.

Mass balance calculations were conducted to compare the bulk analysis results and chamber emission data to evaluate the recovery. It was found that for total VOC, the majority (greater than 80%) of the mass in the applied paint could be accounted for in the subsequent air emissions. The data for the more abundant compounds (e.g., nonane, decane, and undecane) in the paint suggest that there was a margin of error of $\pm 20\%$ in measuring these recoveries.

Due to the relatively high VOC content and fast emission pattern, peak concentrations of total VOC as high as $10,000 \text{ mg/m}^3$ were measured during small chamber emissions tests with a loading factor of $0.5 \text{ m}^2/\text{m}^3$ and an air exchange rate of 0.5 h^{-1} . Over 90% of the VOCs were emitted from the primer and paints during the first 10 hours following application.

A series of tests were performed to evaluate those factors that may affect emissions following application of the coatings. It was found that the type of substrate (glass, wallboard, or pine board) did not have a substantial effect on the emissions with respect to peak concentrations, the emissions profile, or the mass of VOCs emitted from the paint. The emissions from paint applied to bare pine board, a primed board, and a board previously painted with the same paint were quite similar. There were differences among the emissions from the three different paints, but the general patterns of these emissions were similar. The effect of other variables, including film thickness, air velocity at the surface, and air exchange rate, were consistent with theoretical predictions for gas-phase, mass-transfer-controlled emissions.

Results from the testing performed in this study are being used to develop computational methods for estimating the emission rate of total VOCs from solvent-based coating products used indoors. The database on total VOC emission from alkyd paint should also be useful for others involved in model development and validation.

In addition to studying the effects of substrates and other environmental variables on total VOC emissions, small environmental chamber tests were conducted to characterize the emissions of a toxic chemical compound—methyl ethyl ketoxime (MEKO)—from three different alkyd paints. The data resulting from these tests facilitated the development of a set of risk management options for MEKO.

Methyl ethyl ketoxime, another name for 2-butanone oxime or ethyl methyl ketoxime [$\text{CH}_3\text{C}(\text{NOH})\text{C}_2\text{H}_5$, CAS Registry No. 96-29-7], is often used by paint manufacturers as an additive to interior alkyd paints (Weismantel, 1981; Turner, 1988). MEKO has been found to be a moderate eye irritant (Krivanek, 1982). It was also the subject of a Section 4 test rule under the Toxic Substances Control Act (Fed. Regist., 1986). A number of toxicological endpoints have been evaluated by testing conducted under the test rule (Fed. Regist., 1989). MEKO demonstrated carcinogenic activity in long-term inhalation studies, causing liver tumors in both rats and mice.

MEKO acts as an anti-skinning agent (or anti-oxidant) that prevents oxidative drying or skinning of the alkyd paint to improve stability in the can. Usually, the MEKO content in a paint is less than 0.5% (Krivanek, 1982). Due to its relatively high volatility (its boiling point is only 152°C), the majority of the MEKO in the paint is expected to be released into the surrounding indoor air after painting to allow the paint to dry properly on the painted surfaces. The effects of MEKO emissions on indoor air quality (IAQ) and associated exposure risk depend on characteristics such as emission rates and patterns.

Bulk analysis showed that the MEKO content in alkyd paints can be as high as several mg/g. Material balance from the chamber tests indicated that the majority (greater than 68%) of the MEKO in the paint applied was emitted into the air. MEKO emissions occurred almost immediately after each alkyd paint was applied to a pine board. Due to the fast emission pattern, more than 90% of the MEKO emitted was released within 10 hours after painting. The peak concentrations of MEKO in chamber air correlated well with the MEKO content in the paint.

The chamber data were simulated by a first-order decay emission model that assumed that the MEKO emissions were mostly gas-phase mass-transfer-controlled. The first-order decay model was used as an input to the continuous-application source term of an IAQ model to predict indoor MEKO concentrations during and after the application of an alkyd paint in a test house. The predicted test house MEKO concentrations during and after the painting exceeded a suggested indoor exposure limit of 0.1 mg/m^3 for all three paints. The predicted MEKO concentrations also exceeded the lower limit of a suggested sensory irritation range of 4 to 18 mg/m^3 with two of the three paints tested. The elevated MEKO concentrations can last for more

than 10 h after the painting is finished. The model was also used to evaluate and demonstrate the effectiveness of risk reduction options. These options involved selecting lower MEKO paints and establishing higher ventilation levels during painting. The higher ventilation should be maintained about 2 h after the painting is finished to avoid exposure to residual MEKO emissions.

In addition to total VOC and MEKO emissions, the unpleasant “after-odor” which can persist for weeks after application of alkyd paint has been a cause of IAQ concerns. Three different alkyd paints were tested in small environmental chambers to characterize the aldehyde emissions. Emission data indicated that significant amounts of odorous aldehydes (mainly hexanal) were emitted from alkyd paints during the air-drying period. Bulk analyses showed that the alkyd paint itself contained no aldehydes. Mass balance calculations indicated that any aldehydes emitted should have been produced after the paint was applied to a substrate. The aldehydes emission patterns were consistent with the theory that the aldehydes were formed as byproducts from spontaneous autoxidation of unsaturated fatty acids in the applied paint. Chamber data showed that the major volatile byproducts generated by the drying of the alkyd paints were hexanal, propanal, and pentanal. These results facilitated the development of an exposure assessment model for hexanal emissions from drying alkyd paint.

The hexanal emission rate was simulated by a model that assumed that the autoxidation process was controlled by a consecutive first-order reaction mechanism with an initial time lag. The time lag reflects an induction period after painting during which little oxygen is taken up by the alkyd coating. As the final byproduct of a series of consecutive first-order reactions, the hexanal emission rate increases from zero to reach a peak and is followed by a slow decay. This model was confirmed by chamber concentration data. The modeling results also showed that the hexanal emissions were controlled mostly by the chemical reactions that formed intermediates (i.e., the precursors to hexanal production).

An IAQ simulation that used the emission rate model indicated that the hexanal emissions can result in prolonged (several days long) exposure risk to occupants. IAQ simulation indicated that the hexanal concentration due to emissions from an alkyd paint in an indoor application could exceed the reported odor threshold for about 120 hours. The occupant exposure to aldehydes emitted from alkyd paint also could cause sensory irritation and other health concerns.

Latex Paints

The majority (over 85%) of the interior architectural coatings used in the United States are latex paints. Previous testing of latex paint emissions has focused on determining cumulative mass emissions of VOCs. The purpose of previous testing was to assess the effect of these paints on the ambient air and to determine how they contributed to photochemical smog (Brezinski, 1989). NRMRL’s concern has been to estimate people’s time-varying exposure to overall VOC levels and to specific VOCs from indoor latex paints.

The first test series that NRMRL performed on latex paints was integrated into the process of developing and validating its new standard practice for paint testing. NRMRL's small chamber tests indicated that the organic emission patterns of latex paints are very different from those of alkyd paints. Bulk analysis showed that the total VOC content of a commonly used latex paint is usually in the range of 2% to 5%, which is considerably lower than that of alkyd paints (32% to 42%). Instead of alkanes, alkenes, and aromatics, only several polar compounds such as glycols, alcohols, and aldehydes were found in the latex paints.

The chamber test results showed significant differences between the emissions of the same latex paint applied to two different substrates (a stainless steel plate and a gypsum board). The amount of VOCs emitted from the painted stainless steel was 2 to 10 times greater than the amount emitted from the painted gypsum board during the 2-week test period. After the first 2 weeks, over 90% of the VOCs were emitted from the paint on the stainless steel plate but less than 20% had left the gypsum board. The dominant species in the VOCs emitted also changed from ethylene glycol to 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate when stainless steel was replaced with gypsum board. Data analysis by a double-exponential model indicated that the majority of the VOC emissions from the painted stainless steel could be simulated by an evaporation-like phenomenon with fast VOC emissions controlled by gas-phase mass transfer. On the other hand, only a small fraction of the VOCs emitted from the painted gypsum board appeared to be controlled by the evaporation-like drying process. The majority of the VOCs were emitted after the painted gypsum board surface was relatively dry. They were probably dominated by a slow, solid-phase-diffusion-controlled mass transfer process. Long-term experimental data indicated that it may take as long as 3.5 years for all the VOCs to be released from the paint applied to the gypsum board.

The small chamber test results demonstrate that, when the objective of a test is to provide emissions data that are relevant to understanding a paint's emissions behavior in typical indoor environments, one should use "real" substrates such as wood and gypsum board instead of "ideal" substrates such as glass, aluminum, or stainless steel. Proper choice of substrate is therefore crucial for exposure and/or risk assessment studies involving indoor latex paints.

NRMRL also used the small chamber test method to evaluate a relatively new type of interior architectural coating, the so called "low-VOC" latex paint. Low-VOC paint has been used as a substitute for conventional latex paints to avoid indoor air pollution. Low-VOC latex paints are promoted for use in occupied hospitals, extended care facilities, nursing homes, medical facilities, schools, hotels, offices, and homes where extended evacuation of an entire building section for painting would be particularly difficult or undesirable.

Four commercially available low-VOC latex paints were evaluated as substitutes for conventional latex paints. They were evaluated by assessing both their emission characteristics and their performance as interior wall coatings. Bulk analysis indicated that the VOC contents of the four paints (which ranged from 0.01% to 0.3%) were considerably lower than those of conventional latex paints (3% to 5%). EPA Method 24 (40 CFR, 1994) for determining VOC

content (commonly used by paint manufacturers) is not accurate enough to quantify the VOC contents of low-VOC latex paints for quality control and product ranking purposes. Other methods such as EPA Method 311 are more suitable, especially when individual VOC content data are needed.

The fact that “low-VOC” paint had relatively low VOC emissions was confirmed by small chamber emission tests. However, the experimental data also indicated that three of the four low-VOC latex paints tested either had some inferior coating properties or emitted hazardous air pollutants. Significant emissions of several aldehydes (especially formaldehyde, which is a HAP) were detected in emissions from two of the four paints. ASTM methods were used to evaluate the paints’ coating performance including hiding power, scrub resistance, washability, drying time, and yellowing. The results indicated that one of the four low-VOC paints tested showed performance equivalent or superior to that of a conventional latex paint used as control. It was concluded that low-VOC latex paint can be a viable option to replace conventional latex paints for prevention of indoor air pollution. However, certain paints marketed as “low-VOC” may still emit significant quantities of air pollutants, including HAPs. In addition, some of these paints may not have performance characteristics matching those of conventional latex paints.

Due to the use pattern of low-VOC paints proposed by their manufacturers (i.e., partial occupancy during painting and immediate re-occupation after painting), the intimate exposure of sensitive occupants to the low-VOC latex paint emissions (especially to HAPs such as formaldehyde) is of special concern. Long-term environmental chamber tests were performed to characterize the formaldehyde emission profiles of a low-VOC latex paint. The formaldehyde emissions resulted in a sharp increase of formaldehyde concentrations within the chamber, rising to a peak followed by transition to a long-term slow decay. Environmental chamber data indicated that formaldehyde emissions from a low-VOC latex paint can cause very high (several ppm) peak concentrations in the chamber air. When the paint was applied to gypsum board, the formaldehyde emissions decayed very slowly after the initial peak, and the emission lasted for more than a month. The results of these tests allowed for the development of exposure assessment emissions models to facilitate pollution prevention efforts to reduce the amount of formaldehyde released by low-VOC paints.

A semi-empirical first-order decay in-series model was developed to interpret the chamber data. The model characterized the formaldehyde emissions from the paint in three stages: an initial “puff” of instant release, a fast decay, and a final stage of slow decay controlled by a solid-phase diffusion process that can last for more than a month. The semi-empirical model was used to estimate the amount of formaldehyde emitted or remaining in the paint. It also predicted the initial peak concentration of formaldehyde and the time necessary for the formaldehyde to become depleted from paint. Once the activity patterns of building occupants were defined, the model was used for exposure risk assessment.

Additional small chamber tests were performed to investigate the major sources of formaldehyde in the paint. Through comparing emission patterns and modeling outcomes of

different paint formulations, a biocide used to preserve one of the paints was identified as a major source of the formaldehyde emissions. Chamber test results also demonstrated that paint reformulation by replacing the preservative with a different biocide for the particular paint tested resulted in an approximately 55% reduction of formaldehyde emissions. However, since other sources (e.g., additives and binders) of formaldehyde are present in the paint, biocide replacement can reduce only the long-term emissions. Short-term generation of high concentrations of formaldehyde remains a problem. Additional research is needed to identify other potential sources of formaldehyde to completely eliminate formaldehyde emissions from low-VOC paints.

Overall Conclusions

A standard test method was developed to characterize the VOC, including HAP, emissions from interior architectural coatings. The advantages of the developed method and the usefulness of the experimental data it can generate were demonstrated by extensive tests focused on two types of commercially available and commonly used interior architectural coatings: latex and alkyd paints. The experimental data generated by this test method can be used to estimate emission rates, to compare emissions from different products, to predict a paint's effects on IAQ and exposure levels, and to evaluate the effectiveness of risk management options. The test method can also be used as a pollution prevention tool to assist paint manufacturers in reducing or eliminating VOC emissions from their products.

Chapter 1

Introduction

The purpose of the report is to present the results of the U.S. Environmental Protection Agency (EPA) National Risk Management Research Laboratory (NRMRL) Indoor Source Characterization Research Program between 1995 and 1999. The focus of the research program during this period was on emissions of volatile organic compounds (VOCs), including hazardous air pollutants (HAPs), from architectural coatings. Among architectural coatings, the focus of research was mainly on interior paints. Experimental work was conducted at EPA's Small Chamber Source Characterization Facilities by the Indoor Environment Management Branch of the Air Pollution Prevention and Control Division.

Americans spend about 90% of their time indoors. Concentrations of pollutants are often much higher indoors than outdoors. Risk assessment and risk management studies (U.S. EPA 1987, 1990) have found that indoor environmental pollution is among the greatest risks to human health and have advised EPA to address this problem. In response to these studies, EPA established the Indoor Source Characterization Research Program and Experimental Facilities in the late 1980s. Initial research was conducted to characterize organic emission profiles of common indoor materials and products to facilitate the identification of high-risk indoor sources.

In the early 1990s, EPA's Office of Pollution Prevention and Toxics (OPPT) developed an Indoor Air Source Ranking Database (SRD) as part of the Indoor Air Source Characterization Project (Cinalli et al., 1993). The objectives were to categorize product classes and to score and rank product classes based on relative risks. The SRD scores could be used to assign priorities to product classes for further data development and risk screening. Based on formulation data,

emission profiles, use patterns, and health hazard data, architectural coatings, mainly interior paints, were ranked as one of the top priority, high-risk indoor air pollution sources.

Between 1995 and 1999, NRMRL's paint emission characterization research program was devoted to the development, verification, and demonstration of a standard test method for measurement of organic emissions from the two types of commercially available, most commonly used indoor architectural coatings – latex and alkyd paints. A literature survey indicated that there was a lack of reliable and consistent paint emission data needed to develop and evaluate effective risk management options to address exposure risks and health concerns. Further investigation showed that a standard test method was required for testing laboratories, researchers, and paint manufacturers to generate and report emission data that were complete, consistent, and comparable.

The research program produced a standard method for testing organic emissions from paints and six technical papers published in peer-reviewed journals (Chang et al., 1997; Chang et al., 1998; Chang and Guo, 1998; Fortmann et al., 1998; Chang et al., 1999; and Chang et al., 2001). A Standard Practice (Appendix A), based on the standard test method, was developed and submitted to the American Society for Testing and Materials (ASTM) for adoption as the national standard. In 2000, the research program won an Agencywide Pollution Prevention Leadership Award (James Craig Award) for identifying a major source of formaldehyde emissions and successfully preventing air pollution by those formaldehyde emissions with paint reformulation.

This report is divided into 10 chapters and an appendix. Chapters 1 and 2 provide background information:

- Chapter 1, Introduction, summarizes the paint emission research program and the scope, purpose, and organization of this report.
- Chapter 2, Literature Survey, provides background information from selected literature about interior paint consumption data, latex and alkyd paint properties, exposure and health risk concerns, and the need for a standard test protocol.

Chapter 3 focuses on testing methods:

- Chapter 3, Standardized Test Methods, presents the developed standard test method for characterizing organic compounds emitted from paint using small environmental chambers. The coded Standard Practice is provided in the Appendix. This chapter provides a detailed description of the test facilities and the rationale of critical experimental procedures.

Chapters 4, 5, and 6 focus on alkyd paint:

- Chapter 4, Characterization of Emissions of Volatile Organic Compounds from Interior Alkyd Paint, provides experimental data to demonstrate the usefulness of the small chamber test method. Results are presented for a series of tests performed to evaluate factors that may affect organic emissions from interior alkyd paints.
- Chapter 5, Methyl Ethyl Ketoxime (MEKO) Emissions from Alkyd Paint, shows how the standard test method can be used to measure the emission rate of a toxic chemical compound, MEKO, from three different alkyd paints. The chamber data were used to establish an emission model which predicted indoor MEKO concentrations during and after painting. The effectiveness of risk management options, including selection of lower MEKO paints and higher ventilation during painting, was also evaluated by the model.
- Chapter 6, New Findings About Aldehyde Emissions from Alkyd Paint, describes the use of a small chamber test method to characterize the emissions of odorous aldehydes that were produced by autoxidation reactions during the curing (drying) process. This chapter also demonstrates how to employ the chamber data to simulate indoor air quality impact and evaluate exposure risk.

Chapters 7, 8, and 9 focus on latex paint:

- Chapter 7, Substrate Effects on VOC Emissions from a Latex Paint, discusses how the small chamber test method was used to discover the significant effects of two substrates -- a stainless steel plate and a gypsum board -- on the VOC emission rates and patterns from a latex paint.
- Chapter 8, Experimental Work to Evaluate Low-VOC Paints, reports the test results of four commercially available low-VOC latex paints, evaluated as substitutes for conventional latex paints.

- Chapter 9, Experimental Work to Characterize and Reduce Formaldehyde Emissions from Low-VOC Paint, illustrates how the Standard Practice was employed to investigate the contributing sources of formaldehyde emissions from a latex paint. This chapter also demonstrates that small chambers can be used as a tool to conduct pollution prevention research to reduce formaldehyde emissions by paint reformulation.

and

- Chapter 10, References, lists the references cited in the report.

Chapter 2

Literature Survey

This chapter summarizes scientific research pertaining to the measurement of paint emissions and the evaluation of paints' effects on indoor air quality. It provides a context for NRMRL's work on developing standard test practices and it illustrates the fact that these practices met a pressing need within the community of indoor air scientists. The literature survey begins by describing the content of paint; it then summarizes both the patterns of paint use in the United States and the health problems that might result from that use. It concludes by describing the state of small chamber paint emissions testing at the time when NRMRL began its research into standardizing the practice.

Paint Definition and Composition

Paint is a mechanical dispersion of pigments or powders with a liquid or solvent known as a vehicle. The vehicle portion of the paint consists of a non-volatile portion and a volatile portion. After application of a paint, the non-volatile portions of the vehicle (e.g., resin polymers, film-formers, and binders) remain as a film on the coated surface, and the volatile portion evaporates (U.S. EPA, 1997). In addition to pigments and vehicles, paints contain other chemicals (called additives) that enhance their physical properties and make them easier to apply. Wall paint vehicles can be alkyd (solvent/oil-based) or latex (water-based). A paint's vehicle affects the ease with which it can be applied. Most paints are applied by brush, roller or spray.

Solvents perform the following three functions:

- They dissolve the chemicals that, when dried, form the coating's film.

- They dilute the paint solution or emulsion to achieve a proper solids content ratio and viscosity.
- Their evaporation rate controls the paint's rate of drying.

Different types of solvents have varying characteristics:

- **Aliphatic hydrocarbon** solvents are used in alkyd paints. These solvents are petroleum fractions containing mostly aliphatic hydrocarbons with small amounts of aromatic hydrocarbons. These solvents are commonly referred to as naphthas, or mineral spirits. About 75% of the aliphatic hydrocarbons used in alkyd wall paint are mineral spirits (U.S. EPA, 1997).
- In the past, **ethylene glycol** was the organic primary solvent used in latex flat paint. There is a current market trend towards replacing ethylene glycol with propylene glycol in both latex and alkyd paints. This substitution allows manufacturers to develop formulations containing less organic solvent. These new formulations, in turn, have lower and less hazardous organic compound emissions.
- **Glycol ethers and esters** are fully soluble in water. They also aid the freeze-thaw stability, coalescence, and wet-edge control in latex paints. They also make it easier to spread paints on the surface to be coated. These compounds are relatively volatile.
- **Alcohol, ketone, and ester** solvents are used in wall paints. Methyl ethyl ketone and methyl isobutyl ketone are the most common compounds used (NPCA, 1992a).
- **Xylenes** are aromatic hydrocarbons used in alkyd paints. Aromatics have been largely phased out of wall paint use.

Other paint additives that can affect emissions of paint during application include pigments, fillers, thickeners, plasticizers, surfactants, driers, stabilizers, and biocides. Any of these additives can affect emissions through direct emissions or reaction with paint components to produce volatile byproducts that evaporate into the air (U.S. EPA, 1997).

Interior latex paints are usually not considered to be in the same VOC category as alkyd paints because they can be cleaned with water and are non-flammable. Nevertheless, latex paints contain volatile and semivolatile organic chemicals in the range of 3.5% to 9.5% (U.S. EPA, 1997). In general, latex paints are favored over alkyd paints indoors because they release much less odor, cost less, dry faster, and are easier to clean up.

Alkyd paints are used indoors primarily for high-gloss applications or for situations in which a particular surface or condition necessitates their use. For example, alkyd paint may be needed when high moisture resistance is required to minimize mold growth. Alkyd paints are used on a variety of substrates such as metal, plastic, wood, or glass.

Paint Manufacture and Use Statistics

The total volume of alkyd and latex coatings used in the United States has remained around 650 million gallons per year between 1998 and 2000 (U.S. Census, 2000, 2001). More than 60% of this volume was paint applied to indoor surfaces (NPCA, 1992b; U.S. Census, 2000, 2001). Alkyd paint represents a small part (12%) of the total interior wall paint market. Latex paint makes up over 87% of indoor wall paints produced in 2000.

Table 2-1 shows a breakdown of wall paint production between 1997 and 2000. Latex flat paints comprised 98% of all flat wall paints. Latex semi-gloss paints comprise 90% of all semi-gloss wall paints in 2000. For comparison purposes, in 1973, latex flat and latex semi-gloss wall paints comprised 90% and 45% of the flat and semi-gloss wall paint market, respectively. In 1981, those figures were 93% and 70%, respectively, and in 1992 those figures were 97% and 75%, respectively (U.S. Census, 2000, 2001).

Table 2-1. Wall Paint Production by Type from 1997 to 2000

Interior Type	Quantity (thousands of gallons)			
	2000	1999	1998	1997
Alkyd (solvent based)	47,521	51,181	49,514	52,432
Flat	3,239	3,322	3,512	3,727
Gloss	3,216	3,409	3,679	6,067
Semi-gloss	14,122	12,355	11,548	11,803
Primers and Sealers	18,781	19,503	18,796	18,111
Miscellaneous	8,163	12,592	11,979	12,724
Latex (water based)	347,281	339,225	315,636	335,035
Flat	149,252	150,931	137,781	149,115
Semi-gloss	130,872	125,002	114,602	120,635
Primers	33,381	31,581	29,148	26,131
Miscellaneous Stains/Sealers	33,776	31,711	34,105	39,154
Total Interior	394,802	390,406	365,150	387,467

Alkyd paint is composed primarily of organic solvents. Aliphatic and aromatic hydrocarbon solvents make up about half the solvents in alkyd products. These solvents include benzene, toluene, xylene, naphthas, and mineral spirits. The use of oxygenated solvents, including ketones, alcohols, esters, glycol ethers, and glycols, is growing. Ketones (primarily methyl ethyl ketone [MEK], methyl isobutyl ketone [MIBK], and acetone) comprise about 15 % of the coatings solvents market (Markarian, 2000). Alcohols, such as ethanol, butanol, propanol, and methanol, also hold about 15% of the market (Markarian, 2000).

While alkyd paint use is decreasing, emissions from alkyd paints still present a significant potential health risk due to the types of volatile compounds that these emissions contain. Per unit of volume, latex paints contain less hazardous volatile material than alkyd paints do. However, the

volume of latex paints used nationwide each year is extremely large (much larger than the volume of alkyd paints). Thus, widespread exposure to latex paint emissions is still an important source of indoor air pollution. Even though paint composition and consumption are moving away from alkyd paint and towards water-based (latex) paint, the health effects from both types of paint are still under investigation.

Health effects assessments and environmental regulations are focused on the hydrocarbons and hazardous air pollutants (HAPs) contained in both latex and alkyd paint. For example, the hydrocarbons in paint are such significant contributors to photochemical smog formation that California's South Coast Air Quality Management District (SCAQMD) developed legislative standards for paint hydrocarbon content. These standards seek to eliminate 21.8 of the estimated 59 million tons per day of hydrocarbon emission to the ambient air from paint in the South Coast district (Sissell, 1999). At the federal level, the Architectural and Industrial Maintenance (AIM) regulation took effect in 1999. It limits hydrocarbons in architectural coatings and industrial maintenance applications (Markarian, 2000). Both hydrocarbon reductions and HAP regulations are gradually becoming more stringent (Markarian, 2000).

Paint Emissions Exposure and Health Effects

Indoor air exposure of painters and occupants to paint emissions is a health concern (U.S. EPA, 1997). Conventional paints contain VOCs that vaporize, dispersing into the air we breathe. Exposure to VOCs can result in irritation of the eyes, nose, and skin; respiratory problems; headaches; nausea; and dizziness (Pennybaker, 1999; Wieslander et al., 1999). Many of the VOC compounds in paint (such as benzene, formaldehyde, toluene, and xylene) are hazardous. Some of these VOCs are carcinogens or neurotoxins (Pennybaker, 1999; U.S. EPA, 1993).

People are exposed to indoor air pollutants for 90% of the time. They frequently complain about their health or well-being after moving into new or remodeled buildings. However, it can be difficult to interpret the public health significance of these reports since no

federal or state air quality standards exist to limit the exposure of pollutants in non-industrial indoor air. Health threshold limits have not been set for long-term exposure to compounds found in paint emissions. For this reason, the types of compounds and their emission concentration are important to the long-term study of indoor health effects of wall paint exposure.

In Germany, 2 months after a renovated building received occupants, a total VOC concentration of 2,000-3,000 $\mu\text{g}/\text{m}^3$ was measured. After 10 months, the concentration decreased to 900-1,300 $\mu\text{g}/\text{m}^3$ due to intense ventilation (Pitten et al., 2000). It was suggested that even this lower concentration could pose serious threats to well being and health risk to vulnerable occupants such as children with asthma and allergies. Since measurement methods for total VOCs (TVOCs) are not standardized, different measurements of the same emissions can produce significantly different values. Therefore, interpretation of these measurements should proceed only with great caution.

Emissions from newly painted building interiors have been associated with respiratory inflammation, asthma, and eye irritation. Many VOCs, such as terpenes and formaldehyde, are often present in the indoor air of new buildings. However, it is difficult to determine which of these chemicals are causing specific health effects because of the confounding effects of other contemporaneous construction, such as new woodwork and floor coverings. Wieslander and coauthors, from the Swedish Department of Occupational and Environmental Medicine, have reported that these confounding effects prevented them from determining if the solvent-free water-based paints used in renovating and reconstructing a building contributed to the health effects identified in the building's occupants (Wieslander et al., 1999). NRMRL research provides the standard procedures to characterize both the composition and concentration of paint emissions over time. With validated models from NRMRL, health researchers can disentangle the effects of paint emissions from other indoor air emission sources.

Asthma has been reported as a health concern associated with VOC emissions from newly painted indoor surfaces (Wieslander et al., 1997). Wieslander measured exposure to formaldehyde

and VOCs at 62 dwellings. The relationships among exposures, asthma, and clinical signs were calculated by multiple linear or logistic regression, adjusting for possible influence of age, gender, and tobacco smoking. The prevalence of asthma was elevated among subjects with domestic exposure to newly painted surfaces, particularly newly painted wood details and kitchen painting. A significantly increased prevalence of symptoms related to asthma was also observed in relation to workplace exposure to newly painted surfaces. The indoor concentrations of aliphatic compounds (C_8 - C_{11}), butanols, and 2,2,4-trimethyl 1,3-pentanediol diisobutyrate (TPD also known as TXIB) were significantly elevated in newly painted dwellings. The total indoor VOC concentration was about $100 \mu\text{g}/\text{m}^3$ higher in dwellings that had paint coats less than a year old. A significant increase in formaldehyde concentration was observed in dwellings with newly painted wood details. These results indicate that exposure to chemical emissions from indoor paint is related to asthma and that some VOCs may cause inflammatory reactions in the airways (Wieslander et al., 1997).

While many health professionals have focused on symptoms reported by painters and occupants in new or renovated spaces, EPA has investigated the potential risks associated with individual pollutants in the emissions from paint. Using paint emission test results and models from NRMRL, EPA has found that:

- Based on emission chamber work, the approximate 8-hr time weighted average (TWA) for TVOC levels can exceed $2,000 \text{ mg}/\text{m}^3$.
- Xylene emissions from some paint samples approached the exposure levels at which neurologic effects are often seen.
- The high solvent exposures indicated by TVOC measurements from chamber studies lead to concern about the possibility of chronic central nervous system (CNS) effects in professional painters.
- TVOC exposure levels indicate a high likelihood of complaints about indoor air quality during and shortly after painting.

- For MEKO, the risk posed by the Maximum Occupational Exposure (MOE) during typical use presents concerns regarding developmental toxicity health effects.
- The risk of cancer among consumers and professional painters from the inhalation of MEKO during paint application and drying is a concern (U.S. EPA, 1997).

For latex paints, EPA determined that acute and chronic risks exist for professional painters based on exposure to latex paint emissions. They found that:

- TVOC levels are in the range that may result in complaints about indoor air quality. All samples and test conditions in the chamber studies resulted in TVOC levels exceeding 40 mg/m³ as an approximate 24-hr TWA.
- Some latex paint is the source of formaldehyde and acetaldehyde. Neither the exact concentrations of these chemicals nor the exact reason these chemicals are emitted from latex paint had been well characterized by studies completed before 1993.
- Acetaldehyde exposure presents a chronic health risk.
- Acetaldehyde exposure also raises possible concern for cancer risk with risk estimates around 10⁻⁴ based on current potency estimates.
- Formaldehyde exposure raises a marginal concern for cancer risk to professional painters. Risk estimates based on unit risk values using data from emissions tests are around 10⁻⁶ to 10⁻⁴.
- Formaldehyde also presents an acute irritation concern for both consumers and professional painters.

EPA recognizes that the paint industry has been in a state of flux and that it is lowering the VOC content of paint—mainly due to existing regulations that aim to reduce ground-level ozone levels. The marketplace has made a major switch from solvent- to water-based paint over the last 30 years. In addition, the use of mercury as the biocide of choice in paints has been discontinued, based partly on emission tests done by NRMRL (Tichenor et al., 1991). Industry is aware of indoor air problems—for example, some companies have developed and marketed “no-VOC” latex paints that have less odor. Although industry has made significant improvements to address

EPA's concerns, not all the factors in the risk analysis have been addressed, and further research on emissions reduction and health effects is still necessary.

Small Chamber Emissions Testing Procedures

A number of studies have indicated the need for standard test practices for paint emissions. Tichenor and Sparks describe how to manage exposure from indoor air pollutants in residential and office environments. They find that intelligent source management requires knowledge of the sources' emissions characteristics, including their chemical compositions, emission rates, and emission decay rates. As an example, Tichenor describes several scenarios that cover full-time occupancy, part-time occupancy, room ventilation, and room size. For each of these scenarios, Tichenor predicts exposure of occupants to paint emissions. Tichenor concludes that individual exposure to indoor air pollutants is affected by several parameters, including source emission characteristics, source use, occupancy patterns, and ventilation options. Standardized measurement of these parameters is necessary to choose source management options that effectively decrease exposure (Tichenor and Sparks, 1996).

Saarela, in a review of papers describing the emissions from building construction materials, shows that measurement and evaluation of emissions from indoor materials are more meaningful when there are published guidelines for testing and policies for the use of emissions data. According to Saarela, chamber test methods are becoming more important for material classification, product development, and marketing. Therefore, it is important to develop and standardize these measurement methods to ensure that emission measurements, regardless of where in the world they are made, are comparable. There is a need to define all of the testing parameters and analytical procedures in detail so as to generate reliable emissions test data. These data, in turn, are required for developing selection guidelines for building material (Saarela and Sandell, 1991).

Levin first reported on the use of emissions testing for product selection during the design of a large office building (Levin, 1987a, 1987b, 1987c). In 1988, neither environmental chamber testing nor any other product evaluation method provided more than limited data. Even where test data were available, differing methodologies, the testing of non-comparable specimens, or changes in product formulations decreased the data's value for product selection purposes. Levin points out that environmental chamber test results can be used by manufacturers during product development to determine the potential magnitude, composition, and health effects of exposure to their products' emissions. Therefore, Levin found that a standard protocol was needed to guide the emissions testing used for product development, pollution prevention, and exposure assessment programs. Levin presents the basic requirements for a well-designed small environmental chamber, including the pros and cons for several design and monitoring options. He also presents the major obstacles to adequate product documentation and the comparability of test results (Levin, 1989a and b).

In 1991 Levin reviewed the protocols, applications, and problems associated with using environmental chambers to determine VOC emissions from indoor air pollutant sources. His review covered the efforts of NRMRL to develop a small chamber test method that would standardize test procedures. It also covered the consensus American Society for Testing and Materials (ASTM) standard D-5116-90 that NRMRL developed in cooperation with ASTM. Levin compared the small chamber method development work performed by various groups to the large-chamber and whole-house approaches used to characterize emissions from a variety of home construction and decoration materials. Standards development efforts for low- or reduced-VOC products are burdened by the large differences in testing requirements that exist within this diverse group of products. In his review he concludes that the lack of standardized test protocols makes data interpretation and comparison of test results difficult for most product types (Levin, 1991).

Chemical reactions further complicate the procedures for using small chambers to evaluate paint emissions. Many chemical and physical transformations or reactions can occur, both while

the paint is stored in the container and after it is applied to a surface. In-can preservatives and freeze/thaw protectants are incorporated into many paint formulations for quality control purposes. So-called “natural” paints based on casein have been known to deteriorate in the can, resulting in a “spoiled milk” odor after application. Homogeneous and heterogeneous reactions occur after the paint is applied to building interior surfaces. Once there, the change in the composition of the paint due to the evaporation of the volatile contents and the increased concentration of the non-volatile components creates a new chemical balance among the remaining constituents with potential for chemical reactions. One example of this is the large burst in emission of hexanal from latex paints 24 hours after application, as seen in the research described in detail later in this report (Chang and Guo, 1998b).

Chapter 3

Standardized Test Methods for Characterizing Organic Compounds Emitted from Paint Using Small Environmental Chambers

A set of experimental methods was developed for testing the emissions properties of household indoor paints. Those experimental methods have been documented and submitted to ASTM for adoption as a standard practice. “A Proposed Standard Practice for Testing and Sampling of Volatile Organic Compounds (Including Carbonyl Compounds) Emitted from Paint Using Small Environmental Chambers” is included in the appendix of this report. This chapter describes the principal elements of the standard practice and provides detailed information about the background and the rationale of those methods. The goal of the standard practice is to generate quantitative and comparable emissions data. These data, in turn, may be used for:

- Selecting paints for specific purposes
- Establishing paint specifications
- Conducting quality control checks of paint
- Developing new low-emissions paints
- Supporting any future paint labeling programs
- Conducting indoor air quality analyses
- Conducting exposure risk assessments

Test Facilities

The purpose of this section is to provide an overview of the test facilities used for evaluating paint emissions. The design principles and major functions of critical components of the test facilities are also discussed. The small environmental chamber system employed by NRMRL is used as an example. Currently there are no commercially available chamber systems, but investigators can design their own test facilities by following the same principles to suit their

own needs. More technical discussions on small environmental chamber systems can be found in ASTM D5116-97.

The core experimental apparatus with which NRMRL conducts its paint emissions testing is a device called a Small Environmental Test Chamber (“small chamber” for short). A test chamber is a hollow box that may range in size from a few liters to 5 cubic meters. The chamber used at NRMRL is 53 L (0.053 m³) in volume. Chambers with volumes greater than 5 m³ are defined as “large”—they may reach the scale of an entire room. The small chamber, on the other hand, is an apparatus suited to the spatial and financial constraints of a typical laboratory environment. It is also more convenient to operate than a large chamber.

An environmental chamber test facility, designed and operated to determine organic emission rates from paints, should contain the following: test chambers, clean air generation system, monitoring and control systems, sample collection and analysis equipment, and standards generation and calibration systems. Figure 3-1 illustrates a system with two test chambers.

Construction of the Small Chamber

Small environmental test chambers should have non-adsorbent, chemically inert, smooth interior surfaces so as not to adsorb or react with compounds of interest. Care must be taken in their construction to avoid the use of caulks and adhesives that emit or adsorb VOCs. As an example, electropolished stainless steel and glass may be used for interior surfaces. The chamber must have an access door with air-tight, non-adsorbent seals. The chambers must be fitted with inlet and outlet ports for air flow. Ports for temperature and humidity probes may also be required. Ports for sample collection are needed only if the sampling is not conducted in the outlet air.

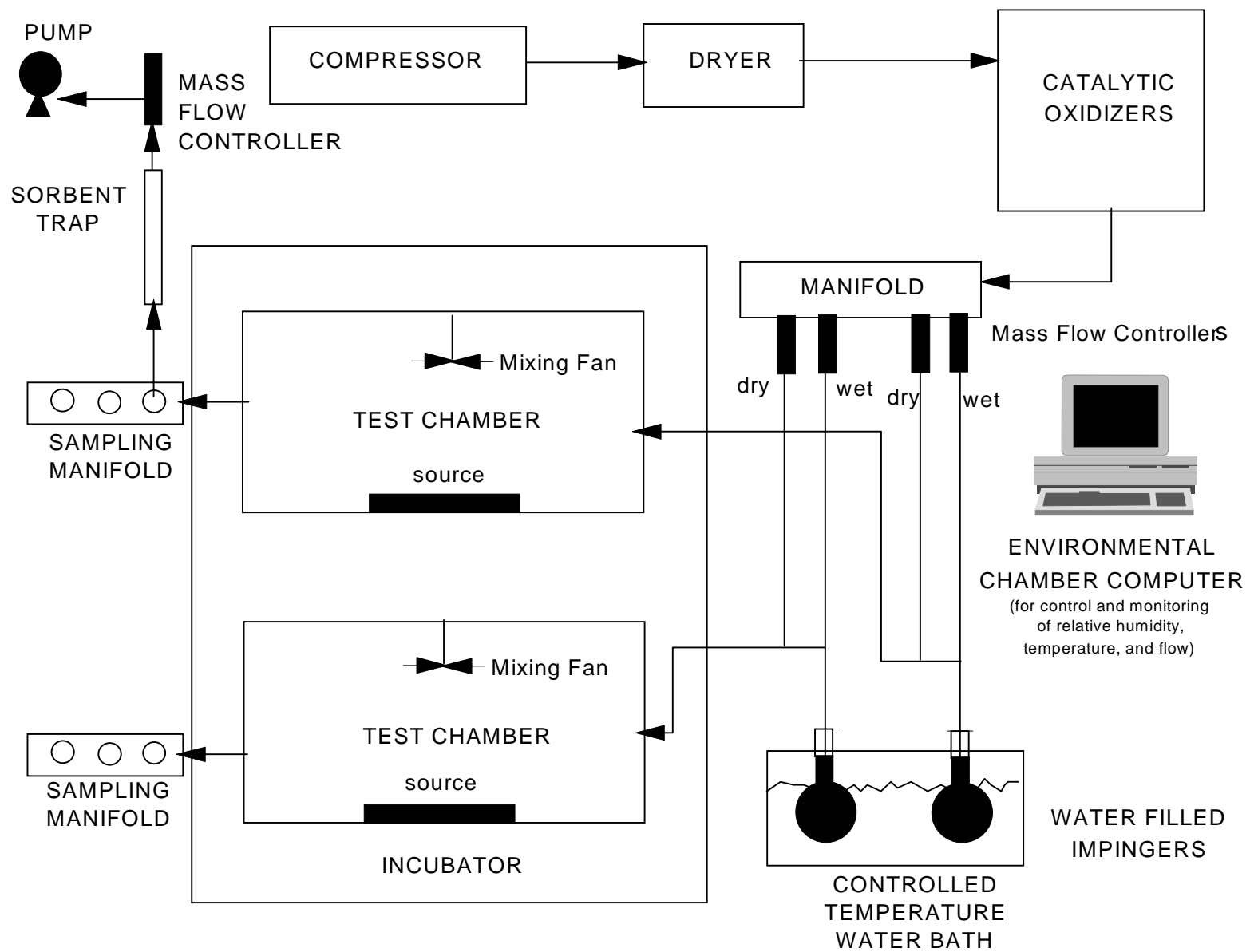


Figure 3-1. Small chamber paint testing facility.

Air Mixing

The chamber and its air-moving components need to be designed to ensure good mixing of the incoming air with the chamber air. While contaminant concentration gradients are expected to exist in the chamber, particularly in the boundary layer near the emissions source, the mixing issue concerns only the uniformity of the concentration in the bulk air inside the chamber. The use of mixing fans and multi-port inlets and outlets are two techniques that have been used successfully to ensure adequate mixing of air in the chamber.

Surface Velocity

The air's velocity near the surface of the material being tested can affect the mass transfer rate. Thus, sources with evaporative emissions (e.g., wet paints) are tested under typical indoor velocities (for example, 5-10 cm/s). A small fan can be used to achieve such velocities. A diffuser should be used to eliminate the calm spot downstream of the fan hub. Velocity measurements can be made with hot wire or hot film anemometers.

Clean Air Generation System

Clean air must be generated and delivered to the chambers to provide adequate background for conducting tests. A typical clean air system might use an oilless compressor drawing in ambient air followed by removal of moisture (for example, using a membrane dryer) and trace organics (for example, by catalytic oxidation units). Other options include gas cylinders or charcoal-filtered outdoor or laboratory air. If granular media (for example, charcoal) are used for control of organics, a particle filter should be used downstream to remove particulate matter. Calculations should be performed to determine the amount of air flow required before a decision is reached on the supply system. For most sources to be tested, extremely clean air is needed. Inlet concentrations should not exceed $2 \mu\text{g}/\text{m}^3$ for any single compound or $10 \mu\text{g}/\text{m}^3$ for the sum of all

VOCs. The purity of the air should be verified by routine analysis of background air samples from a clean chamber.

Temperature Control

Temperature can be controlled by placing the test chambers in incubator cabinets or other controllable constant-temperature environments. The temperature of the inlet air can be controlled by using conditioning coils.

Humidity Control

The humidity of the chamber air is controlled by adding deionized water or high-performance liquid chromatography (HPLC) grade distilled water to the air stream. Injection by syringe pumps followed by heating to vaporize the water can achieve desired humidity levels. Other types of pumps (for example, HPLC) might also provide sufficient accuracy. The chamber air can be humidified by bubbling a portion of the airstream through deionized water at a controlled temperature (for example, in a water bath). The saturated air is then mixed with dry air to achieve the desired humidity. Steam humidification can also be used. Coiled lines inside the constant-temperature environment can be used to equilibrate the inlet temperature before delivery to the test chambers.

Lighting Control

Small chambers are normally operated without lights. If the effect of lighting on emissions is to be determined, appropriate interior illumination should be provided. If the heat generated by lighting is a concern, a transparent chamber lid with a light source placed outside the chamber may be an option.

Environmental Measurement and Control Systems

Measurement and control are required for air flow, temperature, and humidity. Air flow can be automatically monitored and controlled by electronic mass flow controllers, or manual flow control (for example, a needle valve or orifice plate) and measurement (for example, a bubble meter or rotameter) can be used. Temperature can be measured automatically via thermocouples or thermistors; manual dial or stem thermometers can also be used. Humidity control depends on the humidification system employed. If liquid injection is used, water flow is controlled by the pump setting. Control of humidity by saturated air requires temperature control of the water and flow control of the saturated air stream. Humidity can be measured by several types of sensors, including dew point detectors and thin-film capacitors. Temperature and humidity sensors should be located inside the chamber at least 5 cm from the inside wall and near the midpoint between the air inlet and outlet ports.

Automatic Systems

Microcomputer-based measurement and control systems can be used to set air flow rates and monitor temperature, relative humidity, and air flow during the experiments. Analog signals from temperature, relative humidity, and flow sensors are converted to digital data that can be stored by a microcomputer-based system, then processed to engineering units using appropriate calibration factors. In this way, chamber environmental data can be continuously monitored, then compiled and reduced for archival storage or display with minimal operator effort. Automatic systems are also capable of certain control functions. Digital signals can be output to control valves or converted to analog signals and sent out as setpoint signals to mass flow controllers. A graphics overlay program can be used to show current setpoints and measured values on a system schematic displayed on the microcomputer's monitor.

Sample Collection and Analysis

Indoor sources of organic emissions such as paints vary widely in both the strength of their emissions and the type and number of compounds emitted. Differences in emissions rates of several orders of magnitude among sources are not unusual. To characterize organic emissions fully, the sample collection/analysis system must be capable of quantitative collection and analysis of volatile, semi-volatile, polar, and non-polar compounds. Any small chamber sampling and analysis technique or strategy developed must consider the emission characteristics of the specific source being evaluated. The design and operation of sample collection and analysis systems must be appropriate for the organic compounds (and their concentrations) being sampled. Such systems generally include sampling devices, sample collectors, and analytical instruments. The remainder of this section discusses the alternatives available for small chamber sampling and analysis of organic emissions.

Sampling Devices

The exhaust flow (for example, chamber outlet) is normally used as the sampling point, although separate sampling ports in the chamber can be used. A multiport sampling manifold can provide flexibility for duplicate samples. A mixing chamber between the test chamber and the manifold can be used to permit addition and mixing of internal standard gases with the chamber air stream (note that the effective chamber volume should be the sum of the test chamber and the mixing chamber or manifold). Sampling ports with septums are needed if syringe sampling is to be conducted. The sampling system should be constructed of inert material (for example, glass, stainless steel), and the system should be maintained at the same temperature as the test chambers. The exhaust from the sampling system should be ducted into a fume hood, ensuring that any hazardous chemicals emitted by the test materials are isolated from the laboratory environment.

Samples can be drawn into gas-tight syringes, gas chromatograph (GC) sampling loops, evacuated canisters, or through sorbent cartridges using sampling pumps. Gas-tight syringes and closed loops are frequently used when chamber concentrations are high and sample volumes must be small to prevent overloading the analytical instrument. Larger volume samples can be pulled through sorbent cartridges using sampling pumps. Flow rate can be controlled by an electronic mass flow controller (MFC) or other means. The sampling flow rate should be regulated to prevent instabilities in the chamber system flow. Generally, this will require that the sampling flow rate be limited to <50 % of the chamber flow rate. Valves and a vacuum gauge may be incorporated into the system to permit verification of system integrity before samples are drawn. The entire system can be connected to a programmable electronic timer to permit unattended sample collection.

Sample Collectors

Selection of appropriate sample collectors will depend on factors such as boiling point, polarity, and concentration ranges of the compounds of interest, as well as the amount of water vapor in the sample airstream. No single sample collection, concentration, and delivery system will be adequate for all analytes of interest, and the user must understand the limitations of any system used to characterize source emissions. If the sample is collected by way of syringe or closed-loop sampling, it is injected directly into an instrument for analysis. Collection in a sampling bag (for example, Tedlar) or vessel (for example, glass, stainless steel) allows larger samples to be collected and subsequently concentrated and analyzed. For many small chamber evaluations of indoor paints, the fact that some of the compounds of interest are present only at low concentrations requires the concentration of large-volume samples and collection on an appropriate adsorbent medium. Several sorbent materials are available for use, singly or in combination, including activated carbon (charcoal), glass beads, Amborsorb, Tenax (polyphenylene oxide), graphitized carbon, and XAD-2. The selection of the sorbent (or sorbent combination) depends on the compound(s) to be collected. XAD-2 resin can be used to collect compounds considered to be semi- or non-volatile (i.e., boiling points above 180 °C). If sorbent collection is used, the laboratory must be equipped with appropriate storage capabilities. Air-tight glass tubes or chemically inert bags are both appropriate.

Flushing the storage containers with high purity nitrogen prior to use will help ensure their cleanliness. Samples should be stored in a freezer at -20 °C.

When sorbents are used for sample collection, desorption and concentration are necessary. For example, a clamshell oven can be used to thermally desorb sorbent (e.g., Tenax) cartridges with the vapors fed to the concentrator column of a purge and trap concentrator that thermally desorbs the organic compounds. Another example is solvent extraction and dilution of samples collected by charcoal cartridges. If possible, sorbent samples destined for thermal desorption should be processed and analyzed within 48 h of collection. Samples requiring solvent extraction should be processed within 7 to 14 days and analyzed within 40 days of extraction.

Organic Analysis Instrumentation

Several analytical instruments are available for determining the concentration of the organics sampled from the chamber: GCs are the most commonly used. GCs have a wide variety of columns available for separating organic compounds. Gas chromatography separates materials based on the differences between their vapor pressures. Compounds “distill” from a GC column based on how readily they remain in the vapor phase. Capillary columns are generally preferred because they allow more opportunity for compounds to vaporize, condense, and separate from a mixture before exiting the column to the detector. Several detectors can be used depending on the purpose of the test and the compounds of interest. Mass spectrometers (MS) are the most versatile and can be used in the scan mode to identify unknown compounds. When used in the scan mode, a conventional MS has a sensitivity of about 10^{-9} g. An ion trap may have a sensitivity approaching 10^{-12} g in the scan mode. If conventional MS is being used to analyze known compounds, it can be operated in the selective ion mode where its sensitivity increases to 10^{-12} g. MS can be made even more sensitive via negative chemical ionization. Flame ionization detectors (FIDs) are also widely used. They respond to a wide variety of organic compounds and have a sensitivity of 10^{-11} g. Electron capture detectors (ECD) are used for analyzing electronegative compounds (for example, halogenated organics) and have a sensitivity of 10^{-13} g.

Some compounds are not easily measured with GCs; for example, low molecular weight aldehydes. Analysis of these compounds requires other instrumentation. High Performance Liquid Chromatography (HPLC) is one technique used to analyze compounds that are very polar, thermally unstable, or of a high molecular weight. HPLC separations are based on the differential solubility of compounds in a sample. Generally the compounds are derivatized before injection. Once a sample is injected into the HPLC column, compounds dissolve into the solvent pumped through the column. Solubility can be increased by automatically changing the solvent mixture. A variety of packed solid-phase columns are available for separation of different classes of compounds by HPLC. HPLC can be combined with any of several detector types including ultraviolet (UV), visible (VIS), and infrared (IR) spectrometers. Much like gas chromatography, data collected from HPLC analysis using these optical detectors consist of the specific retention time of a compound (which indicates its identity) and the specific detector response (which indicates the quantity of compound in the sample). HPLC can also be coupled with a mass spectrometer (MS) to generate coordinated retention time, concentration, and molecular fingerprint information.

Standards Generation and System Calibration

Calibration gas may be added to the test chamber or sampling manifold from permeation ovens, gas cylinders, or dilution bottles. Calibration (or tracer) gas is added through the test chamber in tests to determine chamber mixing, check for leaks, or to evaluate chamber “sink” effects (i.e., the interactions between pollutants and chamber surfaces). Internal standards for analysis quality control may be added at the head of the sampling system. The internal standard should not be added to the chamber due to the potential for adsorption on the material being tested. Quality control can also be achieved by spiked samples.

Principal Components of the “Standard Practice” for Testing Paint Emissions

The purpose of this section is to provide a detailed description of the experimental procedures included in the standard practice developed by NRMRL for measuring the emission rates of various organic compounds from indoor paints. The practice is applicable to both alkyd and latex paints and primers. The following laboratory procedures are covered in the practice:

- Storing and handling paint prior to analysis
- Analyzing paint in bulk (as a liquid)
- Selecting and preparing a suitable paint substrate
- Applying paint to a substrate to create a test specimen
- Operating the small chamber
- Sampling the specimen's gaseous emissions
- Using instruments to measure chemicals present in the emissions sample
- Analyzing the results of the analytical instruments
- Reporting the experimental results
- Conducting quality assurance/quality control

Storing and Handling Paint Prior to Analysis

The purpose of this procedure is to ensure that the origin and history of each paint tested are clearly documented and that the properties of each paint remain constant throughout the testing process.

To ensure that paint is properly documented, NRMRL recommends that, upon acquiring a new batch of paint, the investigator should record pertinent receipt information on a label attached to the paint. The receipt information includes:

- The date of acquisition
- The source of the paint
- The manufacturer and lot number

Repeatedly opening a large can of paint and extracting small samples from it allows organic compounds to escape from the paint over time. To guard against the possibility of the paint substantially changing in composition while it is being stored for analysis, the investigator should

open the can of paint only once and then immediately divide the paint into aliquots. Each of these aliquots should be intended for a single application of paint to a sample. Although this procedure does not altogether eliminate the problem of uncontrolled vapor loss, it minimizes it and standardizes it across all samples.

It is essential to ensure that the paint within a new can is homogenous before it is divided into aliquots. Over time, unshaken paint may separate into layers with different chemical compositions. Before opening a new paint can and drawing aliquots, the investigator should homogenize the paint; e.g., using a commercial paint shaker. Stainless steel mixing balls may be added to each aliquot to aid in the re-homogenization of the sample immediately before use.

NRMRL investigators store paint and primer aliquots in clean, amber glass vials. The caps of these vials are lined with Teflon[®]. The vials, once filled, are stored at room temperature, away from light. The investigators take care to use them before the expiration of the shelf-life specified by the paint manufacturer. These procedures guard against the deterioration of the paint while it is in storage at the laboratory.

Analyzing Paint in Bulk (As a Liquid)

As a step preliminary to the design and implementation of an emissions test, the bulk composition of the paint in question may be analyzed. NRMRL has adopted a slightly modified version of Method 311 (1996) as its protocol for bulk analysis of paints. NRMRL chose this method because it is a standard EPA method, it has been developed to be flexible, and it provides consistent, comparable, and reproducible results with known performance for a wide variety of materials. NRMRL investigators perform this analysis on an aliquot of every paint investigated in its small chamber research program. By performing a bulk organic compound analysis of every candidate paint, the research program is assured of an initial chemical composition analysis that is consistent, realistic, and comparable to other paint materials tested in the program. The purpose of this analysis is to ascertain the identities and relative abundance of the chemicals likely to be

emitted from the paint into the air. The concentrations of VOCs in the bulk paint can also be used with an emissions source model to predict VOC concentrations in the small chamber during testing. All of this information is useful in the design of the emissions test because it gives the investigators choices of the kinds of sampling and analytical techniques that can be used. Proper sampling techniques, for example, vary depending upon the kinds and concentrations of chemicals one expects to be present.

Investigators proceed with this method by diluting an aliquot of paint with an appropriate solvent and centrifuging the mixture to remove solid matter. Potentially suitable solvents for this step include dimethylformamide, methylene chloride (for alkyd paints), or acetone or acetonitrile (for latex paints). The investigator may need to perform several initial tests to ascertain which solvent most effectively dilutes the paint. The interested reader may refer directly to Method 311 (1996) for more specific details on procedures and quality control checks for analyzing the supernatant.

A portion of the supernatant is injected into a GC/MS. The investigator's choice of GC column and operating procedure depends on his or her initial assumptions about what kind of chemicals are present in the supernatant. One general rule serves as a foundation for these assumptions and is particularly noteworthy. It is that alkyd primers and paints primarily contain relatively non-polar aromatic and aliphatic VOCs, while latex paints contain a significant amount of polar compounds (e.g., glycols, glycol ethers, and alcohols).

Selecting and Preparing a Suitable Paint Substrate

The purpose of NRMRL's procedures for selecting and preparing paint substrates is to provide a realistic, representative, and adequate substrate for painting. Traditional substrates, such as glass, stainless steel, and aluminum plates, are not realistic and representative for interior paints. NRMRL suggests that investigators use common indoor materials such as gypsum board and wood. A substrate should be sufficiently large to generate adequate loading, it should not be

contaminated, and its edges should be sealed (with sodium silicate or Teflon[®] tape) to minimize edge effects.

The investigator should procure substrate material and cut it to an appropriate size (which depends on the loading rate desired in the small chamber). For example, a 16 by 16 cm square of substrate (a 0.0256 m² square) would provide a loading of 0.48 m²/m³ for a small chamber with a volume of 0.053 m³. The surface of the substrate must be smooth to facilitate the application of a smooth layer of paint—when necessary, an appropriate abrasive should be used to produce a smooth surface before the paint is applied.

The sides of the substrate (which are neither painted nor counted as part of the substrate's area) should be sealed to prevent them from allowing the escape of organic vapors. At NRMRL, this is accomplished by coating them with a solution of sodium silicate.

Until the substrates are ready to be used, they must be protected from exposure to ambient organic vapors which might contaminate them and bias emissions tests. Two ways of doing this are: (1) storing the substrate in an area with very low levels of VOCs, or if this is not possible, (2) storing the substrate in an airtight container. For at least 24 hours prior to use, the substrates should be conditioned in the small chamber at exactly the temperature and humidity at which the sampling will be conducted. The purpose of this process is to make sure that the substrate is already “conditioned” (in steady state with its environment) when it is painted.

Applying Paint to a Substrate to Create a Test Specimen

One of the key objectives of NRMRL's paint testing practice is to apply paint in a controlled fashion that is realistic, quantifiable, and comparable. The first part of this objective is to apply paint in a way that is realistic—that is, in a manner similar to how it would be applied by actual house painters. In addition, the results of the emissions tests should be analyzed with reference to a quantitative measurement of the mass of paint applied. Finally, in order for different

tests to be comparable, they must consistently involve approximately the same mass and thickness of paint.

With these goals in mind, NRMRL recommends using a roller or a brush under most circumstances and a slit applicator for perfectly smooth surfaces such as glass. The slit applicator will not leave a smooth coat on rougher surfaces such as gypsum board or wood because it cannot compensate for valleys and ridges in the substrate. NRMRL did not find other applicators to be particularly useful. Electronic applicators, for example, are expensive and they do not produce a film that is sufficiently smooth and reproducible. Another applicator device, the spray gun, is impractical given the small size of the test specimen, the waste from overspray, and the loss of VOCs during spraying.

An investigator should begin the paint application process by determining the mass of paint to be applied, using product data listed on the paint container label. One can calculate the mass of paint needed using the spreading rate (ft²/gal.), the density of the paint, and the area to be painted:

$$M_p = \frac{A(D_p)}{SR} \quad (3-1)$$

Where:

- M_p = target mass of paint to be applied (g),
- A = area of the substrate (cm²),
- D_p = density of the paint (g/mL), and
- SR = spreading rate, generally listed on container or data sheet as ft²/gal. (cm²/mL).

The appropriate mass of paint can then be weighed out into a tray. At this point, the uncoated substrate should also be weighed. The paint may then be applied to the substrate using the roller (or alternate applicator). Once application is complete, the amount of paint applied is determined either by measuring the increase in the substrate's weight or the decrease in the roller

and tray's weight. The final weight of the paint applied should be within 10% of the target application amount originally calculated.

Operating the Small Chamber

The purpose of this phase of NRMRL's standard practice is to provide a controlled environment for conducting emissions testing that can reflect common indoor air conditions.

Therefore, NRMRL recommends that the small chamber should be set to maintain an environment within the following operating ranges:

Temperature:	20 to 25 °C
Air Exchange Rate:	0.3 to 2 h ⁻¹
Air Speed:	5 to 10 cm/s
Loading:	0.3 to 1.5 m ² /m ³

The relative humidity of inlet air should be maintained at 50% unless defined otherwise. These operating ranges were chosen to match the actual conditions under which interior house painting is likely to take place.

Prior to each use, the environmental test chamber, the sampling manifold, and all other internal hardware should be cleaned to remove any chemicals which may have adhered over the course of previous use. NRMRL uses alkaline detergent and deionized water as its cleaning agents. The environmental conditions used for testing should be maintained for 24 hours prior to the beginning of the test.

Sampling the Specimen's Gaseous Emissions

This part of the chamber operation and sample collection is critical to a successful emissions evaluation. With new or unusual coating materials, some trial and error experimentation

may be necessary to develop a method that ensures complete and accurate collection of the paint emissions.

Sampling Protocol

As a test progresses, the experimenter may need to periodically adjust the airflow controllers for the sorbent tubes and the length of sampling. At any given time, an important goal of sampling is to deliver a precisely measured volume of air to the sampling media that conveys an optimal mass of VOCs. An optimal mass of VOCs is one that is small enough to avoid overloading the sorbent yet large enough to be detected by the analytical instrument.

During the early stages of a test, VOC emissions are often so high that they quickly overwhelm sampling media. These conditions necessitate the collection of small sample volumes, which can be difficult to measure precisely. The precision of the measurement of small sample volumes should be maximized by adjusting the two settings that determine it: rate of airflow and period of sampling. These two settings must multiply to produce the required sample volume—particular settings should be chosen so as to maximize the *overall* precision of the measured sample volume. Typical small-sample collection times range from 5 to 10 minutes. In some cases, the investigator may choose to sample through two sorbent cartridges in series. A separate analysis of the second sorbent cartridge will reveal whether or not overloading (i.e., “breakthrough”) has occurred in the first cartridge.

Higher airflow rates and longer sample collection periods may be required in later stages of the test as the concentrations of VOCs decrease in the chamber air. Again, the objective of the selection of sampling time and flow rate is to collect sufficient organic material to be within the sensitivity range of the analysis procedure yet avoid exceeding the sampling media capacity. The total sampling flow rate must be less than 50% of the airflow from the chamber (e.g., less than 220 mL/min for a 53 L chamber with an air exchange rate of 0.5 h⁻¹).

Air samples should be collected at predefined intervals during the test. The duration of the test and the frequency of sample collection will vary, since they are determined by the objectives of the test. A high frequency of sampling will be required if the objective of the test is to develop or evaluate source emission models. A lower frequency of sampling may be appropriate for other test objectives. If resources are available, NRMRL's recommended sampling times for collection of data for model development during a 2-week test with alkyd paint are at 0.25, 0.5, 1, 1.5, 2, 4, 6, 8, 10, 12, 24, 48, 72, 96, 144, 192, 264, and 336 hours following the start of the test. NRMRL's recommended sampling times during a 2-week test with latex paint are at 2, 4, 8, 12, 24, 48, 72, 96, 144, 192, 264, and 336 hours following the start of the test. After sampling, one should carefully seal sample tubes and record sampling flow rates and durations on them.

Sampling Media

During the first 10 to 20 hours after application of an alkyd primer or paint, air samples for determination of VOCs may need to be collected on charcoal cartridges. These cartridges, if used, are subsequently extracted with organic solvent. The use of charcoal cartridges may be necessary because the very high concentrations of the VOCs in initial emissions can preclude the use of Tenax and thermal desorption methods (due to the potential for breakthrough on the sorbent media and overloading of the analytical instrument). Charcoal cartridge extracts can be diluted if the emission sample concentration is too high for the analysis equipment. After the initial drying period, the concentrations of VOCs will decrease to levels amenable to collection on Tenax.

In addition to charcoal and Tenax sampling, air samples may be collected on silica gel for the measurement of certain carbonyl-bearing compounds. A fourth sampling method (which allows collection of aldehydes) uses silica gel coated with acidified 2,4-dinitrophenylhydrazine (DNPH). Samples collected on sorbent media or DNPH-silica gel cartridges should be analyzed as soon as possible and no later than 30 days after collection. If they must be stored, they should be refrigerated at lower than 4 °C.

Using Instruments to Measure Chemicals Present in the Emissions Sample

The overall goal of the analysis of an emissions sample is to determine the amount and kind of VOCs that the sample contains. Examples of the sampling and analysis methods followed by NRMRL for monitoring paint emissions include:

- GC/MS is used for compound identification. GC/MS is applicable to samples collected on charcoal, Tenax, and silica gel. Compound identification is based on chromatographic retention time and molecular fragmentation patterns from the unknown compounds. Compound identification is confirmed by comparison with the National Institute of Standards and Technology (NIST) mass spectral library data base. The advantage of GC/MS is its ability to use an established data base of mass spectra for a variety of organic compounds.
- GC/FID is used for quantification of non-polar compounds such as alkanes, alkenes, and aromatic compounds. Like GC/MS, GC/FID can be used to quantify compounds collected on charcoal, Tenax, and silica gel. Compound identification is confirmed using relative chromatographic retention times determined by GC/MS. Compound quantification is based on calibration using at least five standard concentrations covering the quantification range of the instrument. GC/FID has the advantages of being less expensive than GC/MS and able to quantify compounds over a wider concentration range.
- HPLC/UV is used for identification and quantification of polar compounds such as ketones and aldehyde that GC/FID cannot determine easily. HPLC is applicable to samples collected on dinitrophenylhydrazene (DNPH). Compound quantification is based on calibration with nine carbonyl compounds: formaldehyde, acetaldehyde, propanal, benzaldehyde, pentanal, m-tolualdehyde, methyl isobutyl ketone, hexanal, and heptanal. Additional carbonyl compounds can be analyzed with this technique if the appropriate standards are available for calibration.

Analyzing the Results of the Analytical Instruments

One of the purposes of analyzing the results of the sampling instruments is to convert the analytical results (chamber concentrations) into emission rates (ERs) and emission factors (EFs).

The two technical terms commonly used to describe the rate of emissions from indoor materials, ER and EF, are related as follows:

$$ER = A(EF) \quad (3-2)$$

where:

ER	=	emission rate (mg h ⁻¹),
A	=	source area (m ²), and
EF	=	emission factor (mg m ⁻² h ⁻¹).

Calculating VOC Emission Rates and Emission Factors

Once the chamber concentration data are obtained, the emission factor can be calculated by three methods:

- Direct calculation from individual data points (Equation 3-3)
- Direct calculation from the time/concentration profile (Equations 3-4 and 3-5)
- Using an explicit chamber model (Equation 3-6)

Selection of the most suitable method or methods depends on several factors, such as the type of source, data quality, and sampling frequency.

If the emissions rate is nearly constant and the chamber has reached steady state, the emission factor can be calculated from a single data point:

$$EF = C_s \left(\frac{N}{L} \right) \quad (3-3)$$

where:

C_s	=	steady state chamber concentration (mg m^{-3}),
N	=	air change rate (h^{-1}), and
L	=	loading factor (m^{-1}).

Note that this method may have significant error if the emission rate is not constant and/or the chamber has not reached steady state.

Where the emission rate is not constant but there are enough chamber concentration vs. time data points (for example, 10 or more) and the data are relatively smooth, a time-dependent emission factor profile can be obtained directly from the concentration data:

$$EF(t_i) = \frac{\frac{\Delta C_i}{\Delta t_i} + NC_i}{L} \quad (3-4)$$

where:

$EF(t_i)$	=	emission factor at time t_i (mg h^{-1}),
C_i	=	chamber concentration at time t_i (mg m^{-3}), and
$\Delta C_i/\Delta t_i$	=	the slope of the time/concentration curve at time t_i ($\text{mg m}^{-3} \text{ h}^{-1}$).

The slope is approximated by the average of the slopes of two adjacent intervals:

$$\Delta C_i / \Delta t_i = \frac{\frac{C_i - C_{i-1}}{t_i - t_{i-1}} + \frac{C_{i+1} - C_i}{t_{i+1} - t_i}}{2} \quad (3-5)$$

Thus, if there are $n + 1$ data points for concentration, $n - 1$ emission factor values may be obtained by this method. Such calculations can be easily carried out in an electronic worksheet. Before making the calculations, make sure that replicate samples are replaced by the average values to avoid dividing by zero.

The results from this method (Equations 3-4 and 3-5) are independent of any source emission models. Additional benefits of these direct calculations include the fact that the results can be used to check the validity of a chosen model, and that they can help select the most appropriate model for further data analysis (see the following section on Using Emissions Models). Note that differential methods such as this have the potential for high levels of uncertainty. If there are sufficient data points but the random error is significant, a data smoothing process can be considered before using this method.

Using Emissions Models

Another technique that NRMRL used to analyze the sampling results is to relate those data to models of paint emission. Those mathematical models are useful for the purpose of predicting (i.e., interpolating and extrapolating) emission rates, calculating their effect on indoor air quality (when used as input to an indoor air quality model), and conducting exposure risk assessment. When existing models, usually of an empirical nature, are not adequate, NRMRL develops new mathematical simulations (as illustrated in Chapters 5 to 9) of the time-dependent concentration data.